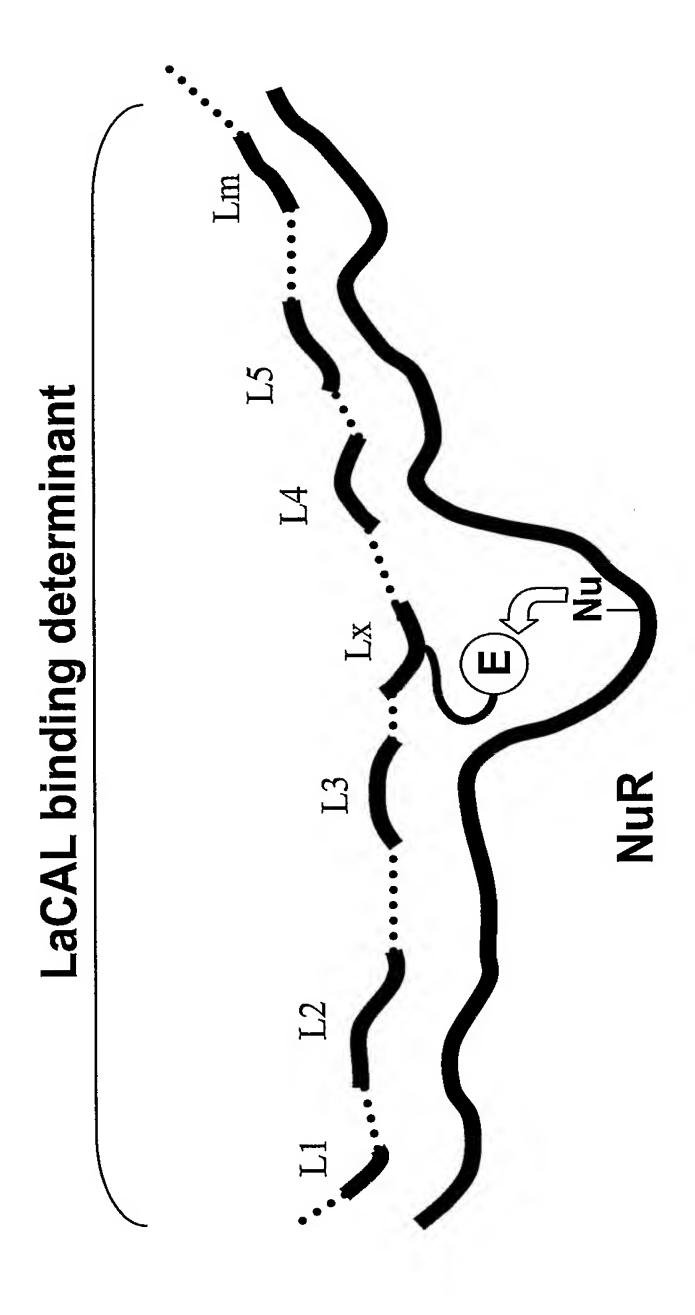
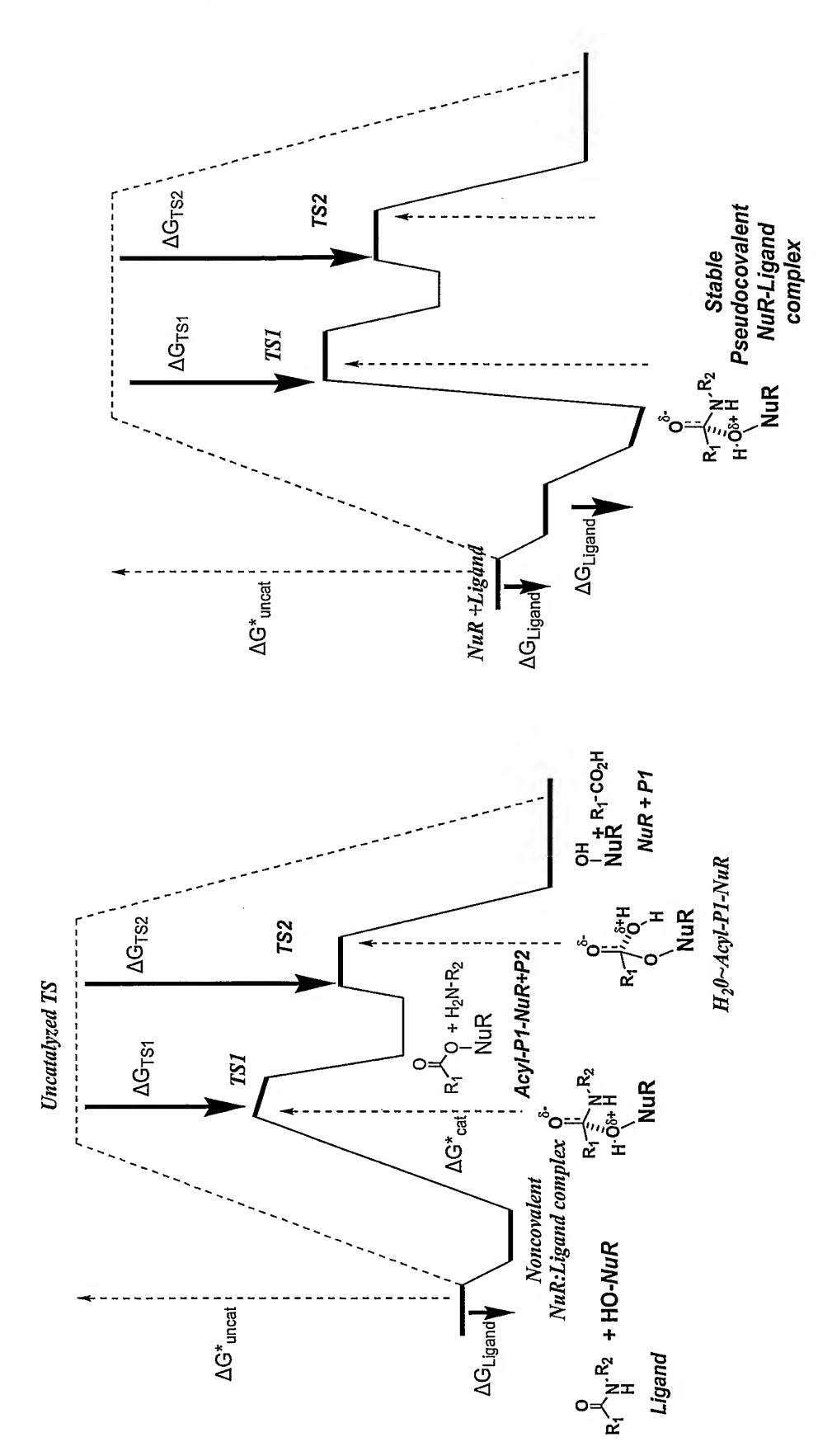
Fig 2



Catalysis and covalent binding energies of proteins



L' =sulfhydryl group of Cys

General structure of LaCAL

L'-Y"-Y, Example 1

L' =
$$\beta$$
-carboxyl group of Asp
$$\begin{bmatrix} O=C \\ \uparrow & \longleftarrow Y'' = \text{amide bond} \\ Y' = \text{ethyl amine group} \\ Y' = \text{phosphonate monophenylester group} \\ Y = \text{phosphonate monophenylester group}$$

L'-Y"-Y, Example 3

L'-Y"-Y, Example 2

$$L' = \varepsilon\text{-amino group of Lys} \begin{bmatrix} V'' = \gamma\text{-maleimidobutyryl group} \\ V'' = \gamma\text{-maleimidobutyl group} \\ V'' = \gamma\text{-malei$$

LaCAL Z-R pair: Example 1

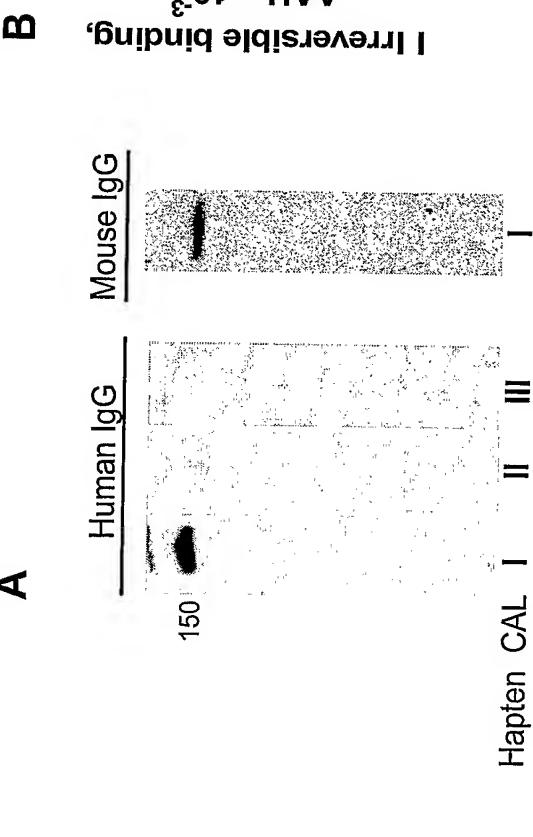
Fig 5E

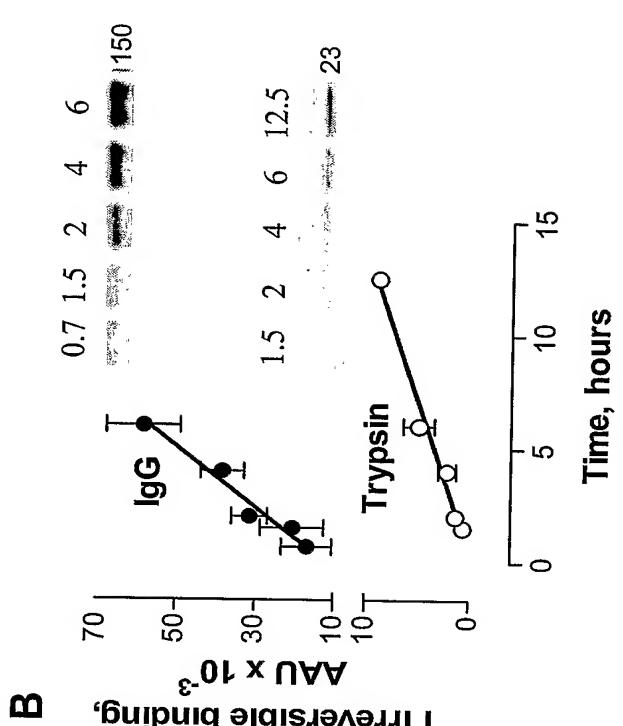
Fig 5D

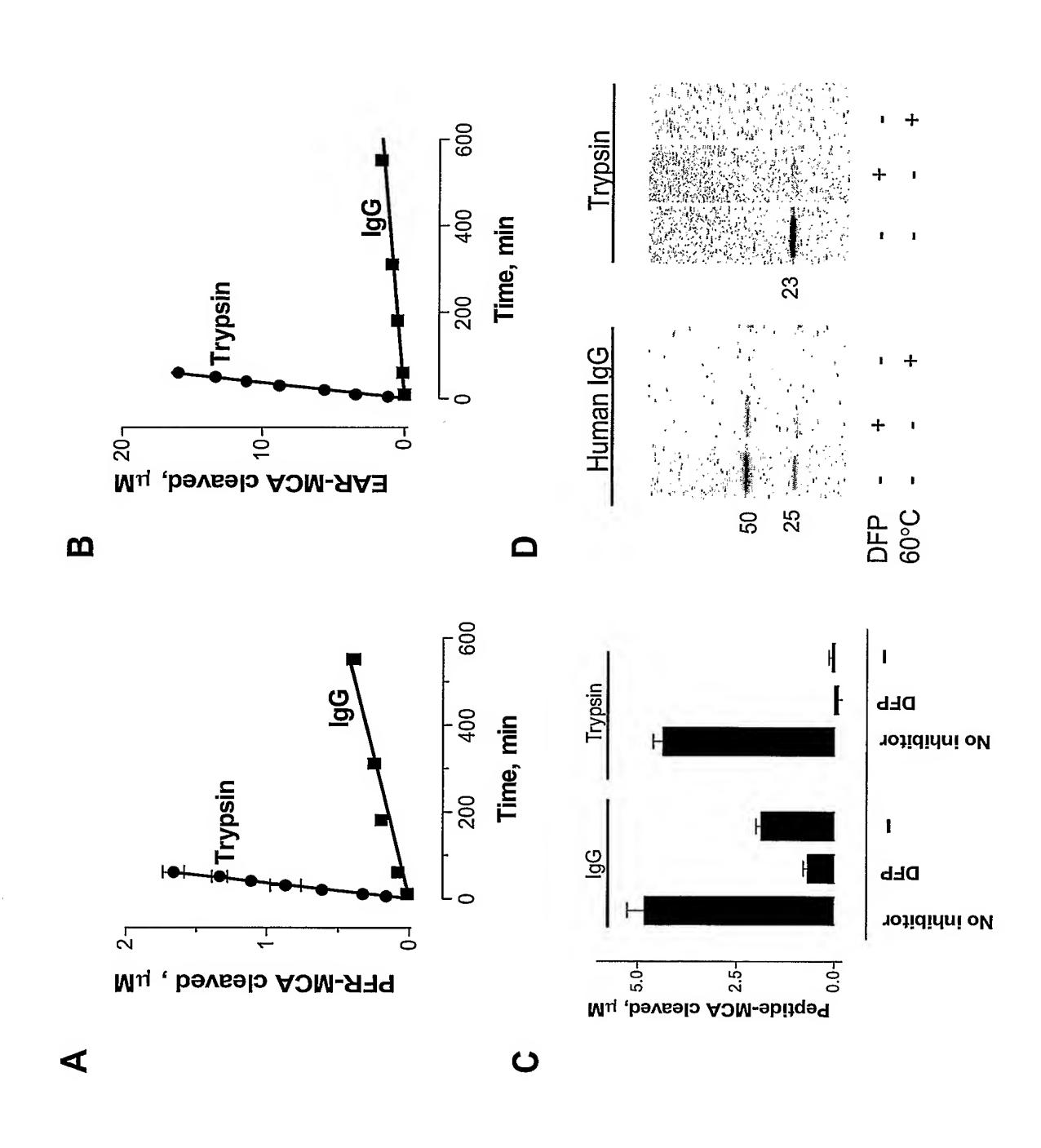
A. Electron withdrawing substituents with peptide extension

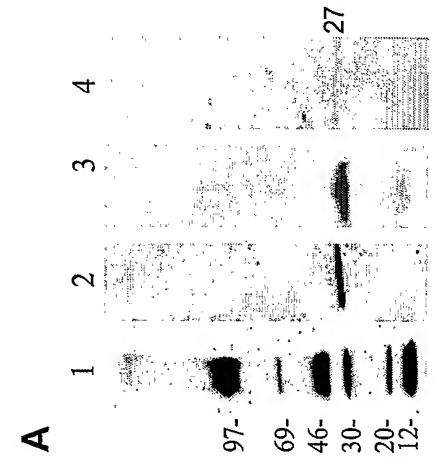
B. Electron donating substituents with peptide extension

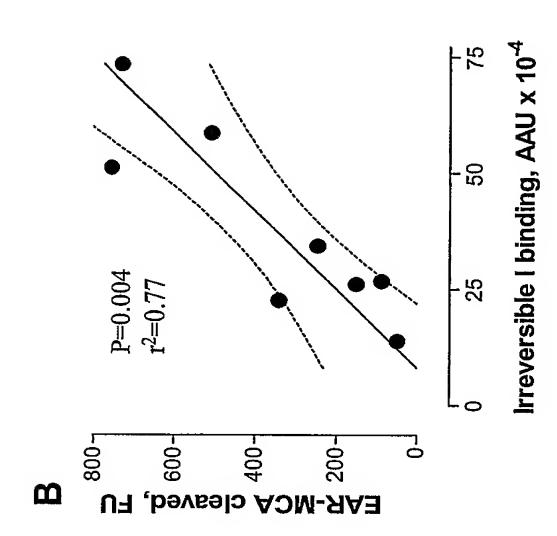
Fig 6

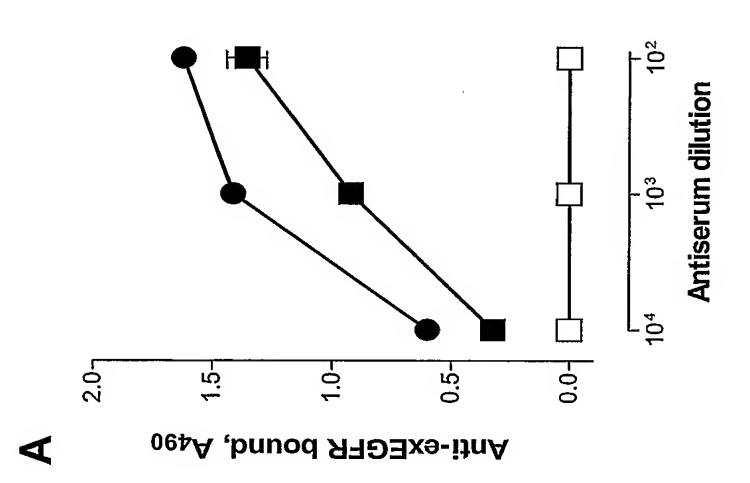


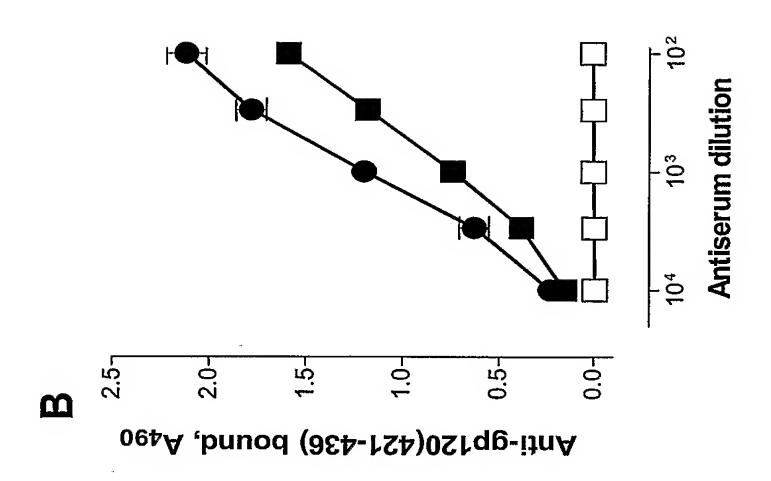












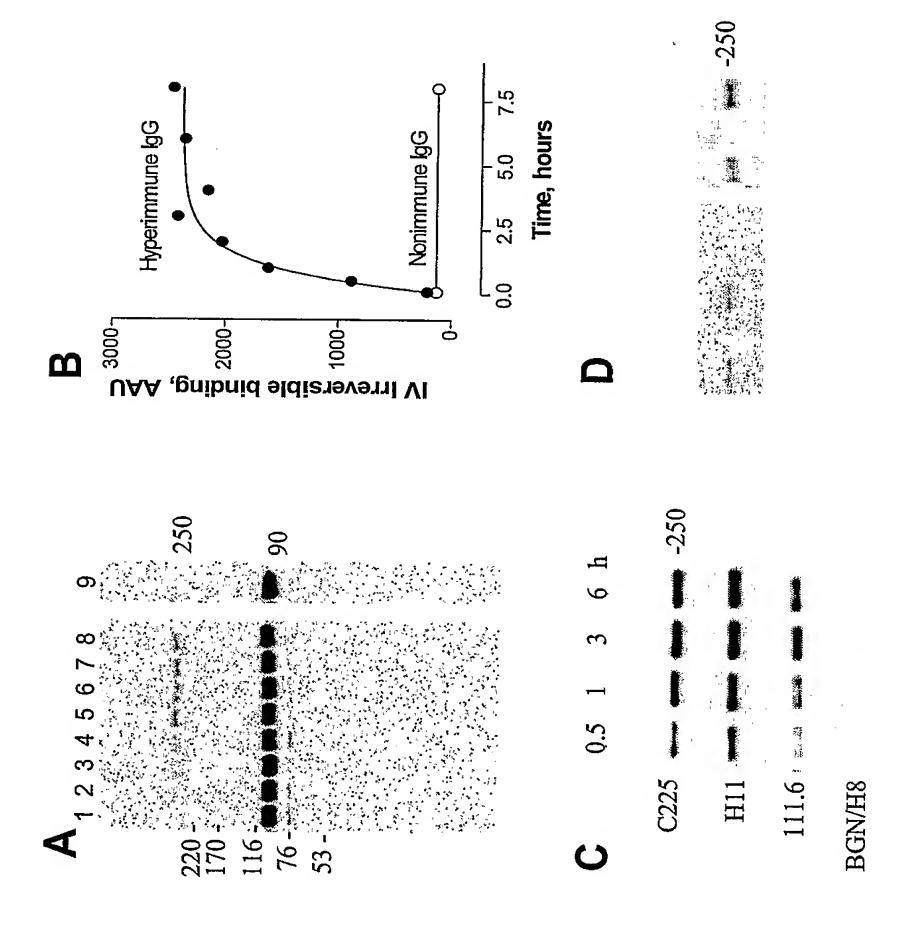
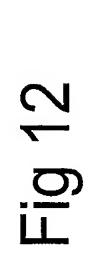
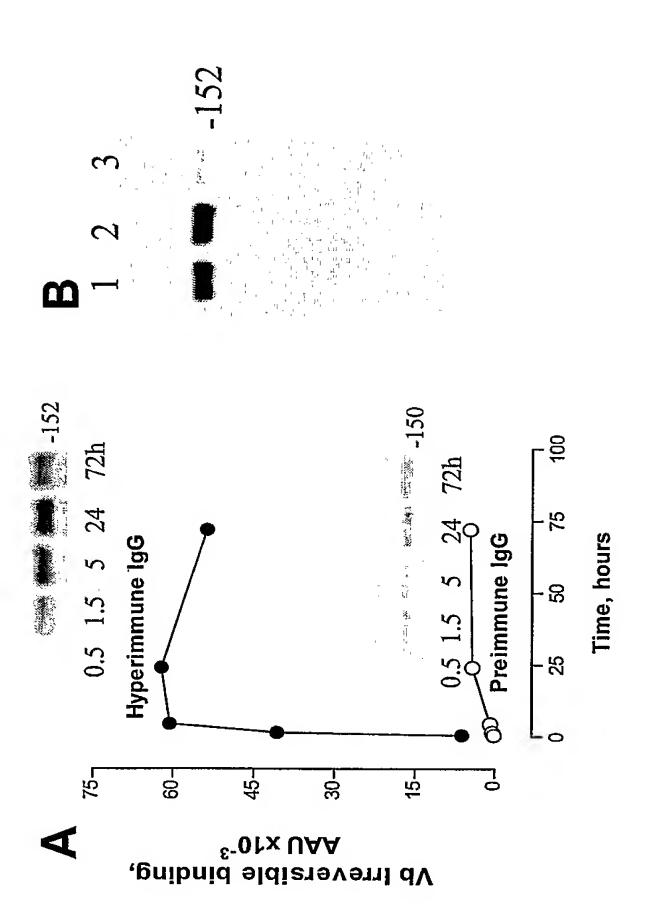


Fig 11





HN NH₂

R-N R-O

1: R = 6-(D-biotinamido)hexanoyl
2: R = O-succinimidylsuberyl

ΙŹ

Lys-Tyr-Leu-Asn-Ser-Ile-Leu-Asn-NH₂ R-His-Ser-Asp-Ala-Val-Phe-Thr-Asp-Asn-Tyr-Thr-Arg-Leu-Arg-Lys-Gln-Met-Ala-Val—N

3: R = D-biotinyl

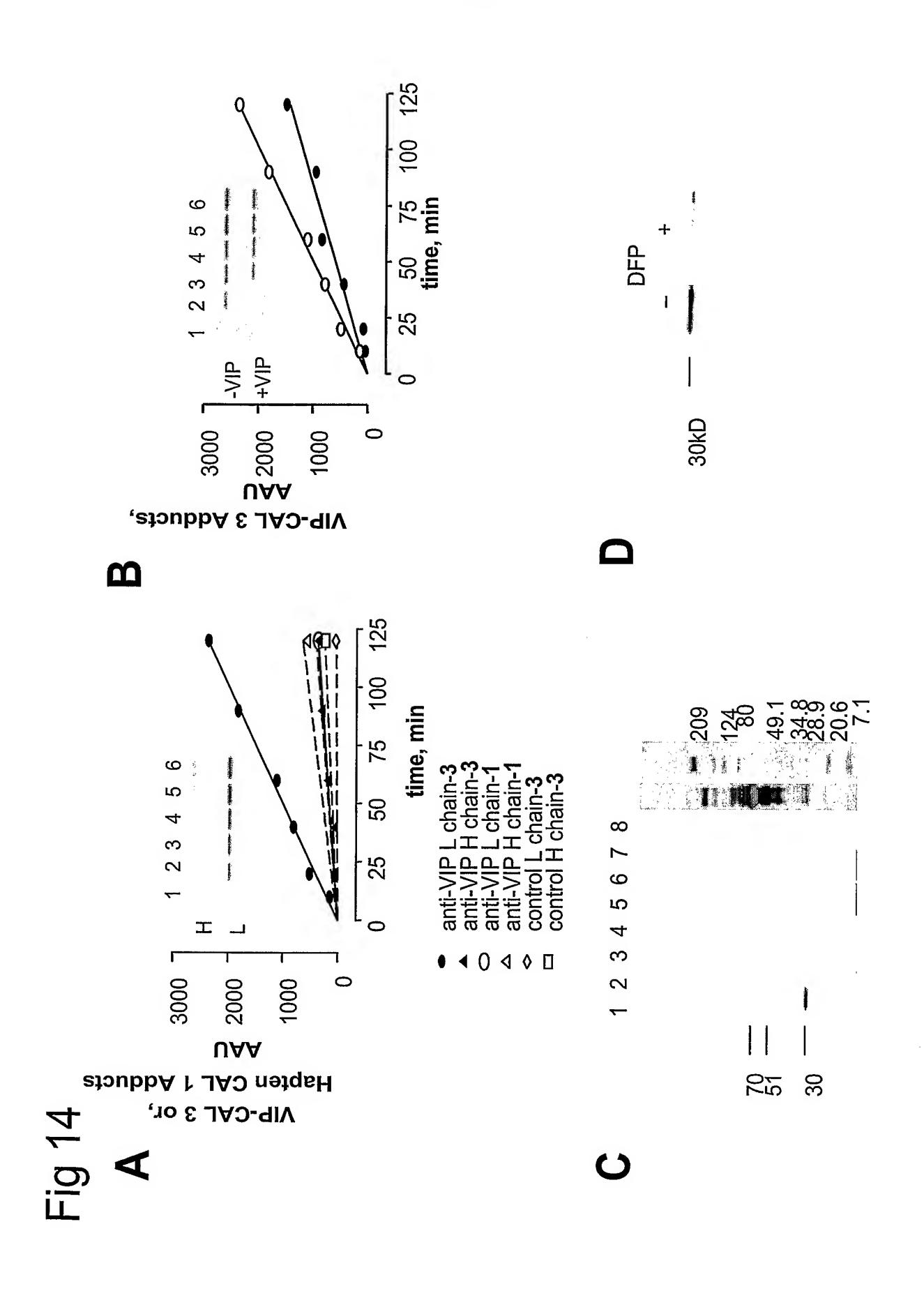
Fmoc-Asn(Trt)—N—

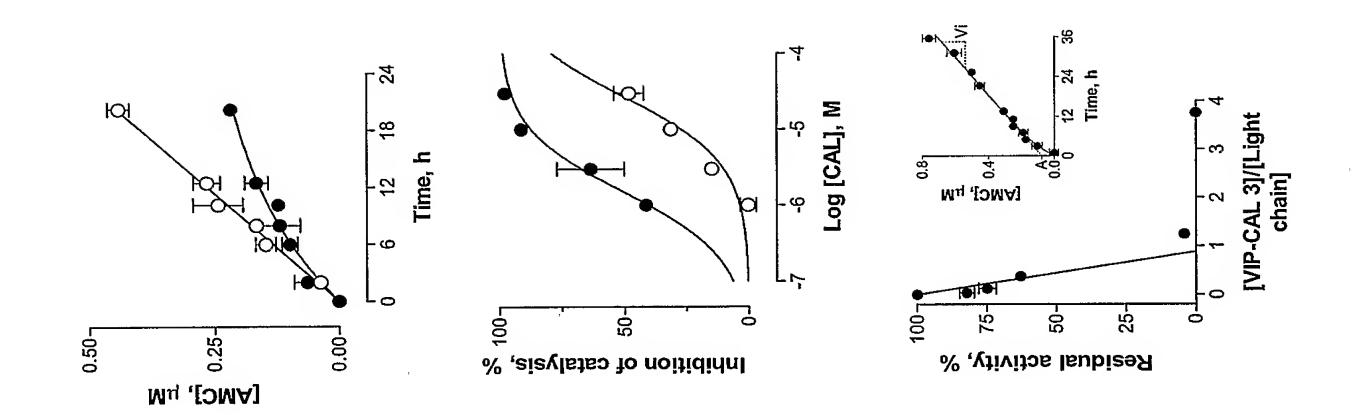
R₁-His-Ser-Asp-Ala-Val-Phe-Thr-Asp-Asn-Tyr-Thr-Arg-Leu-Arg-Lys-Gin-Met-Ala-Val-Lys-Lys-Tyr-Leu-Asn-Ser-Ile-Leu-Ash Boc tBuO tBuO tBuO tBu Pmc Boc tBu tBų

ii,iii 4a (R₁=Fmoc; R₂=Mtt) \downarrow 4b (R₁=D-biotinyl; R₂=Mtt) \downarrow 4c (R₁=D-biotinyl; R₂=H)

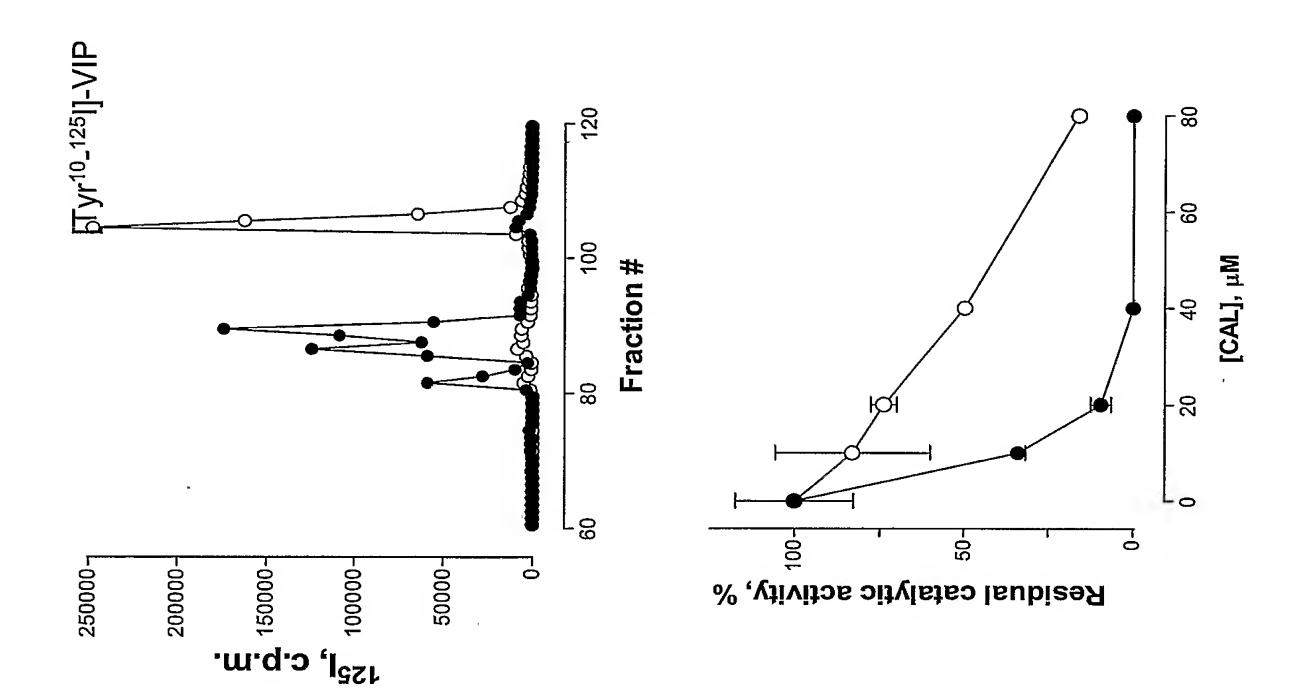
: Solid support

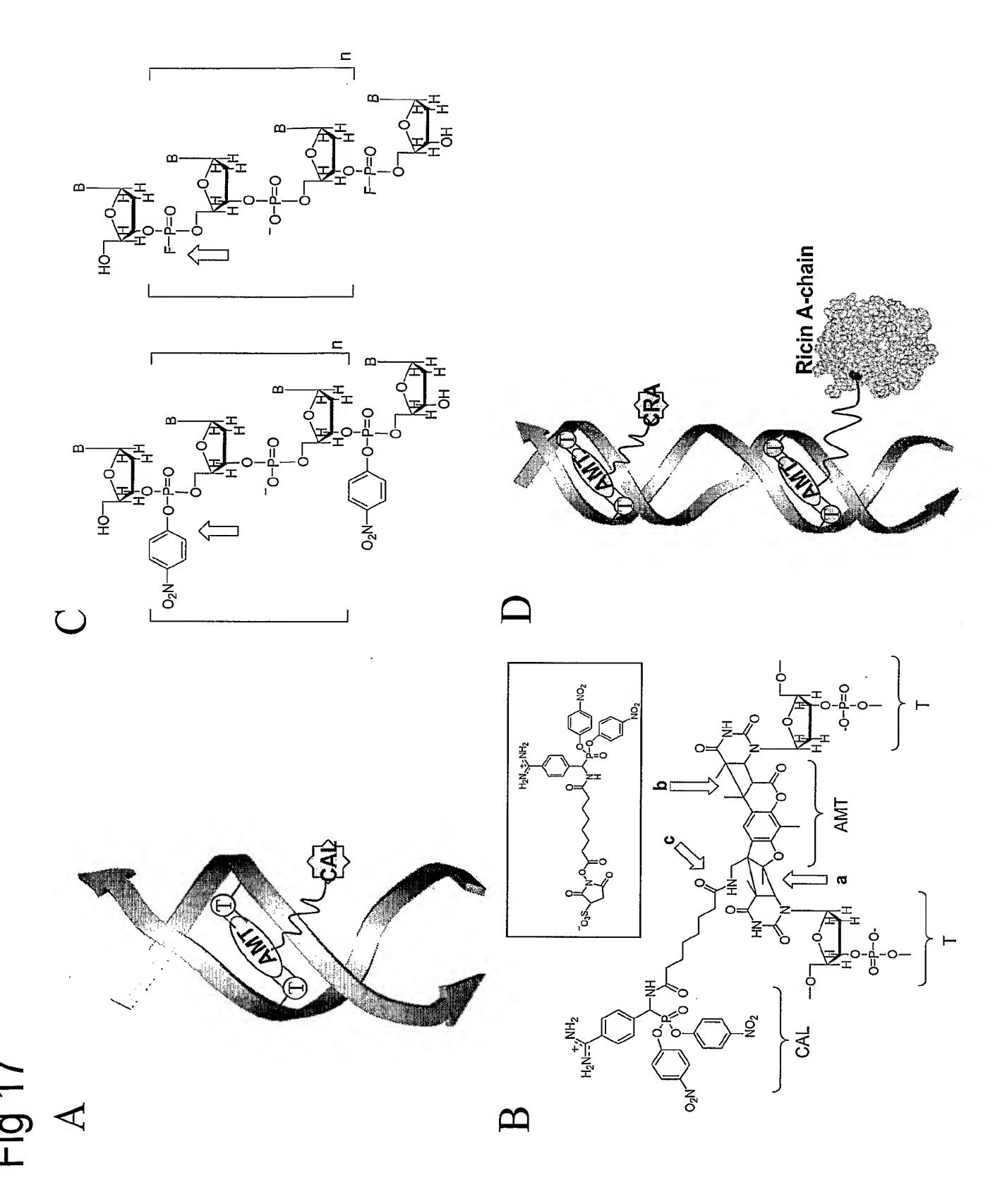
 Ω





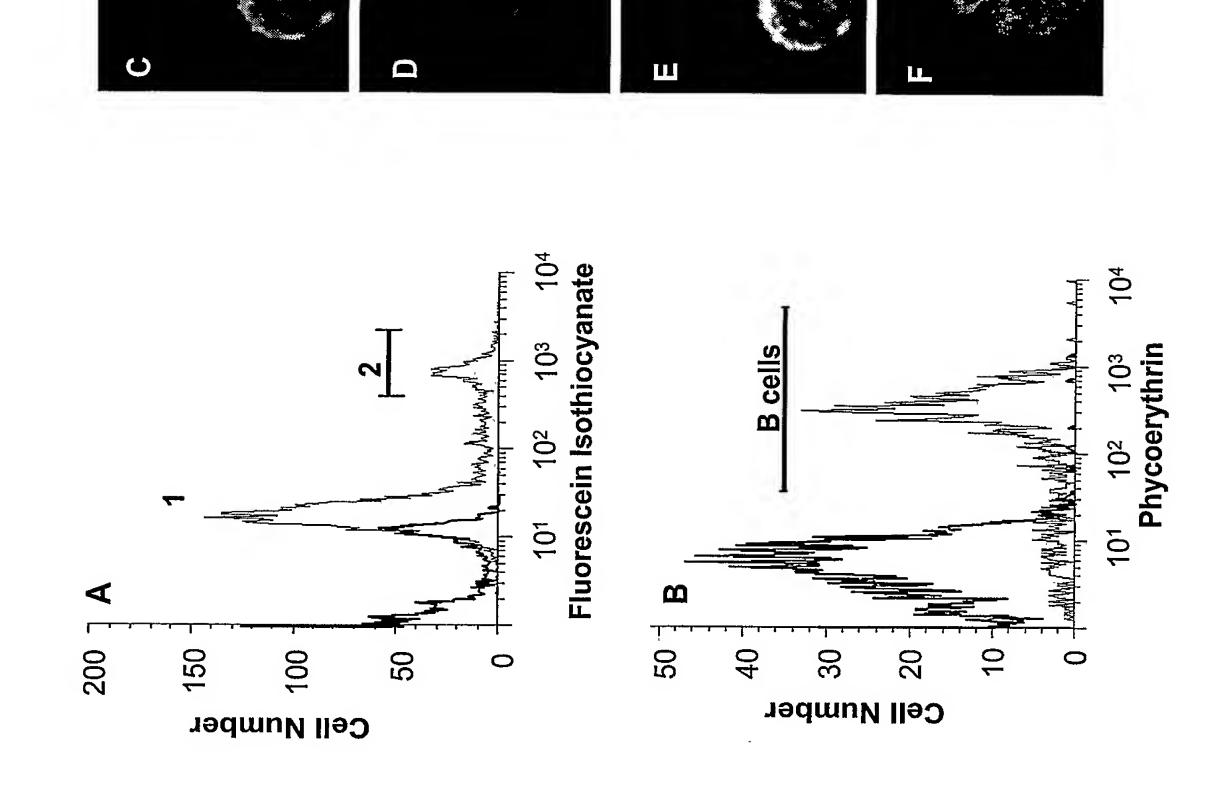
 M





pyruvyl VIP-CRA

Fig 20



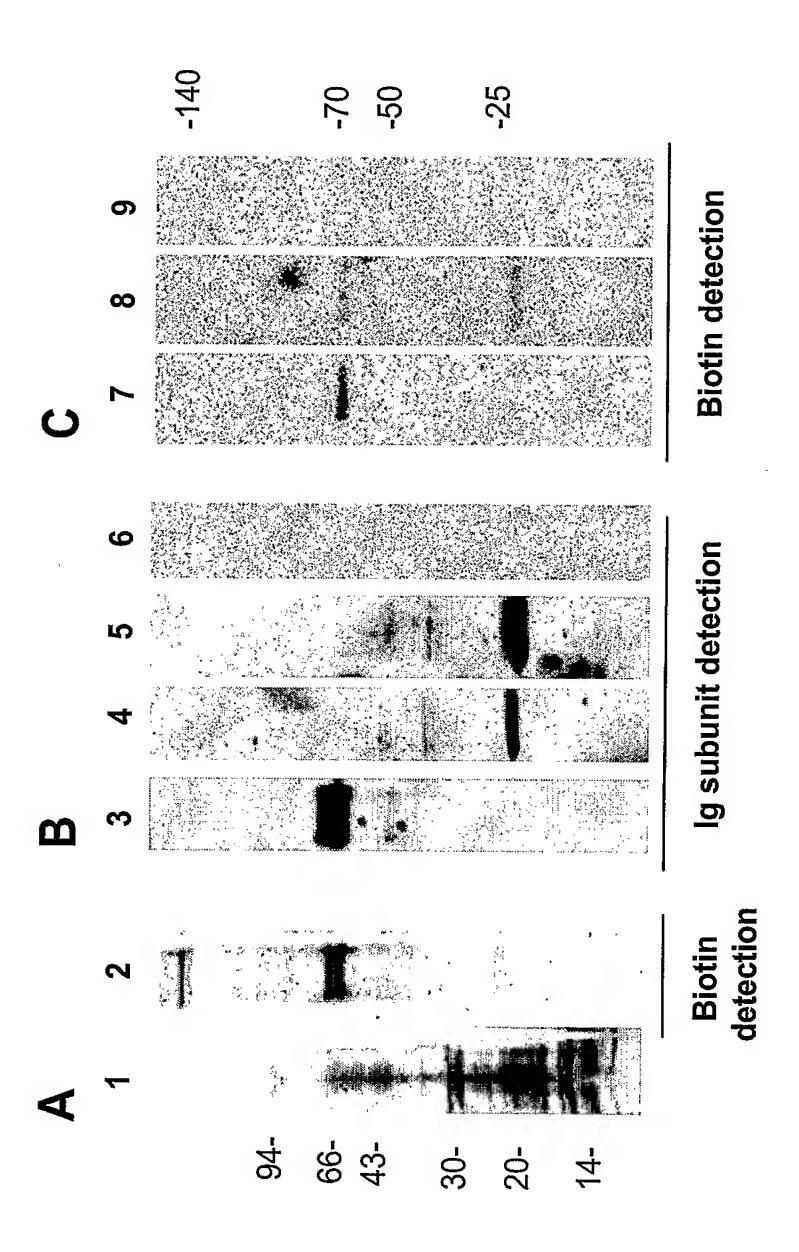
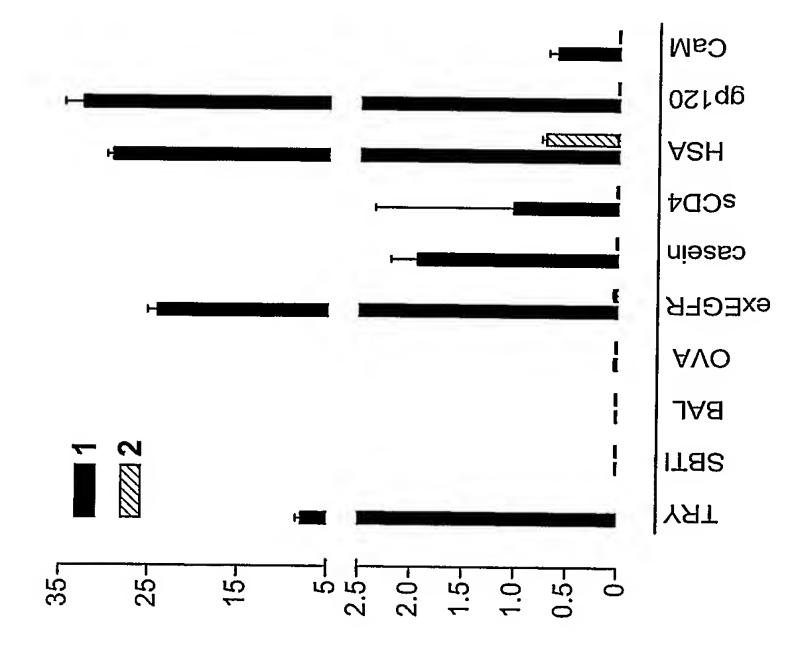
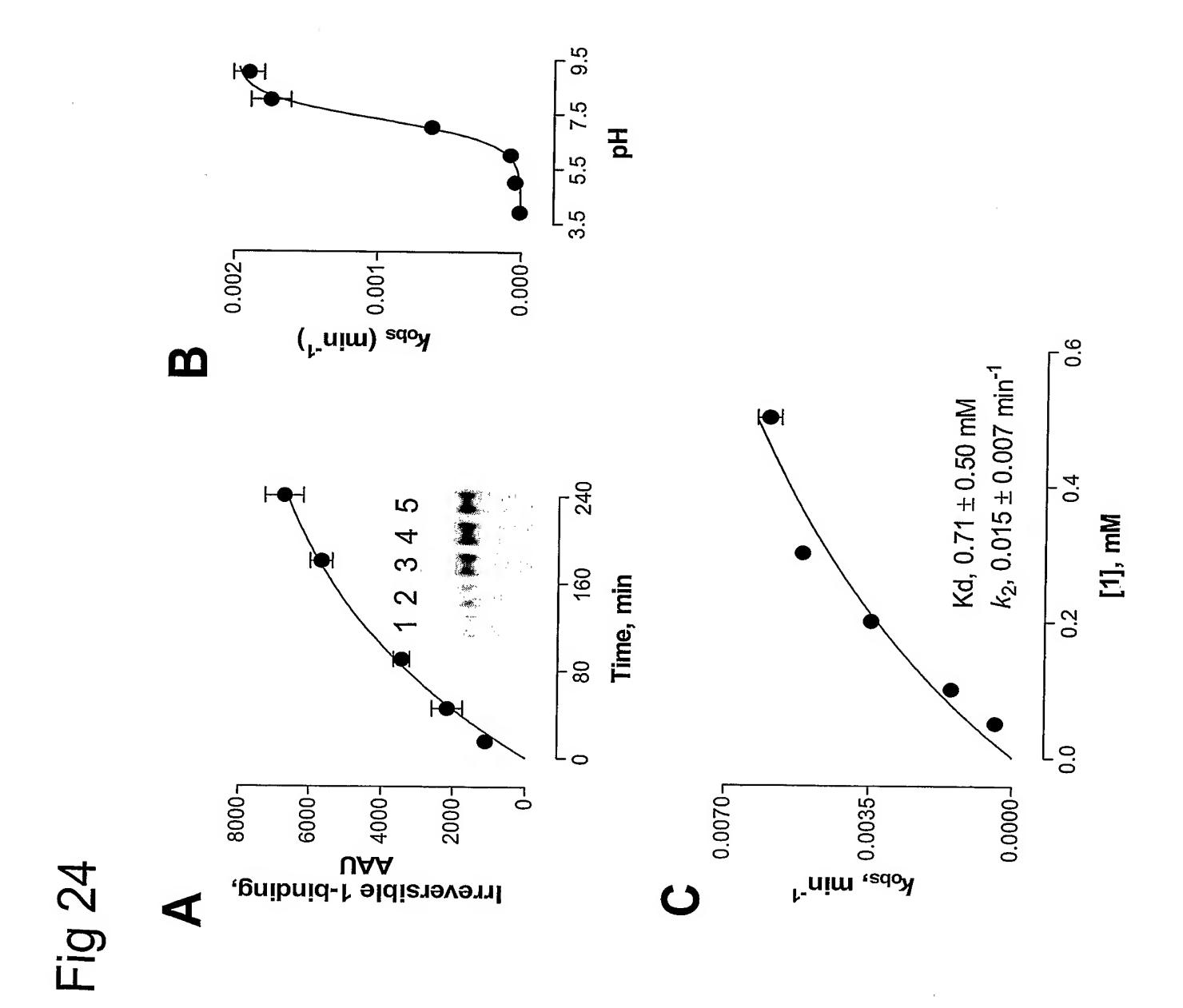


Fig 21

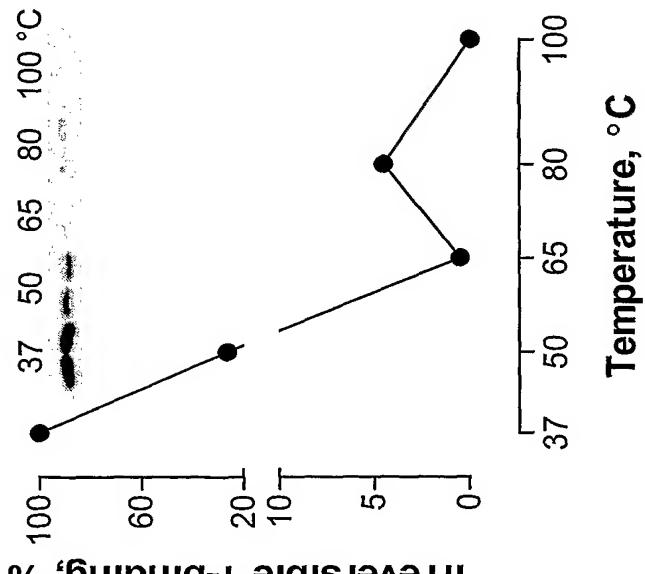
lrreversible 1- or 2-binding, AAU \times 10^3



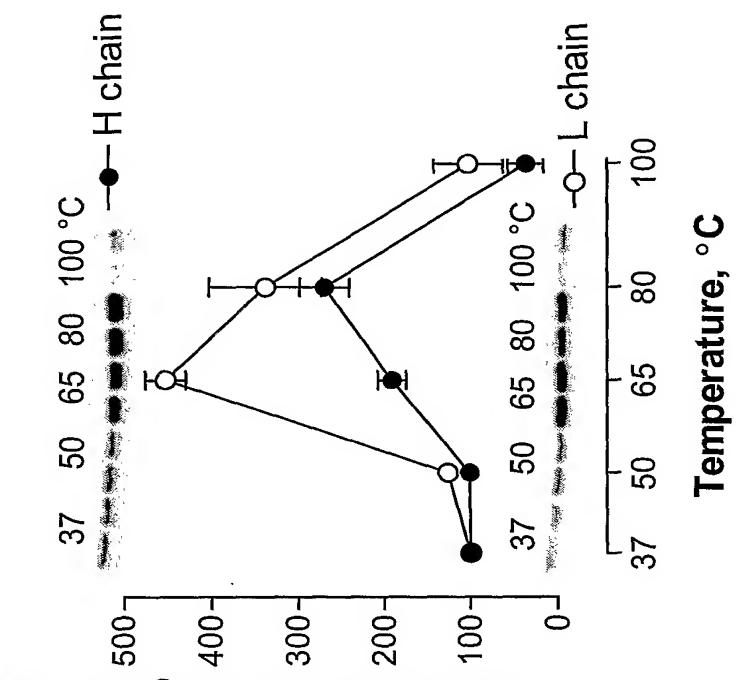




Irreversible 1-binding, %



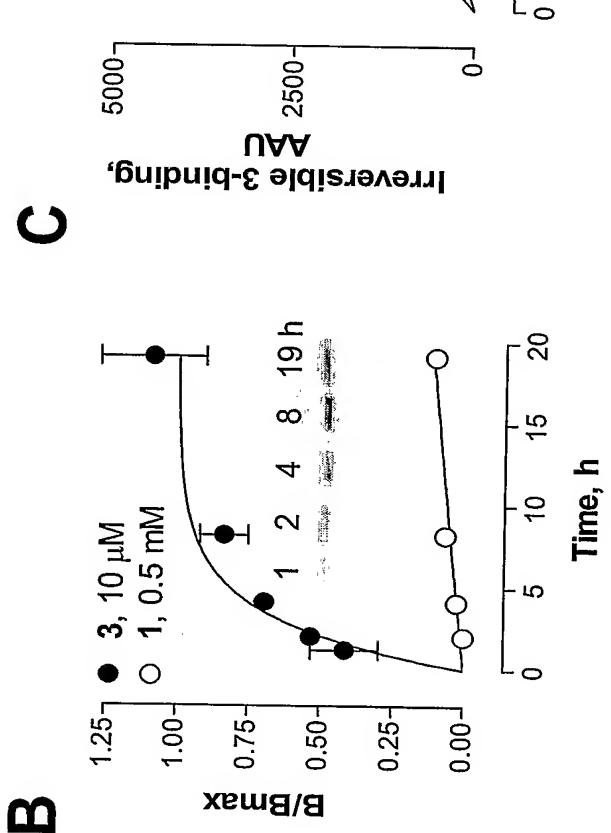
Irreversible 1-binding, %



-Lys-Tyr-Leu-Asn-Ser-lle-Leu-Asn-NH₂ HZ IZ

R-His-Ser-Asp-Ala-Val-Phe-Thr-Asp-Asn-Tyr-Thr-Arg-Leu-Arg-Lys-Gln-Met-Ala-Val—N

3: R = D-biotinyl



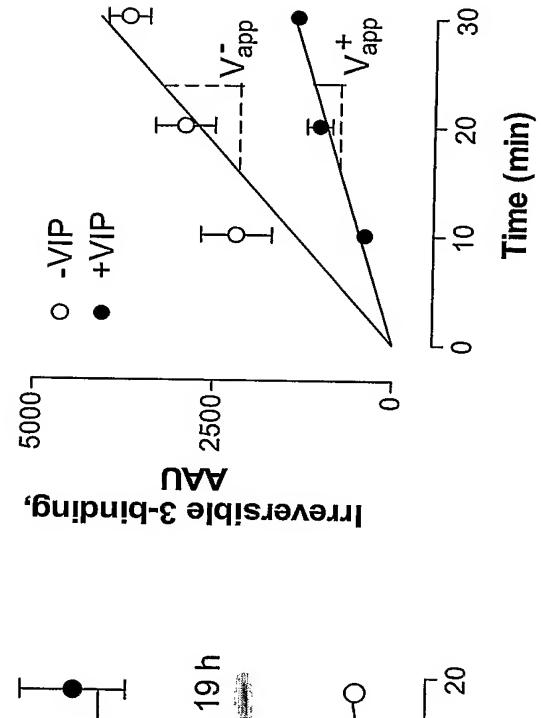
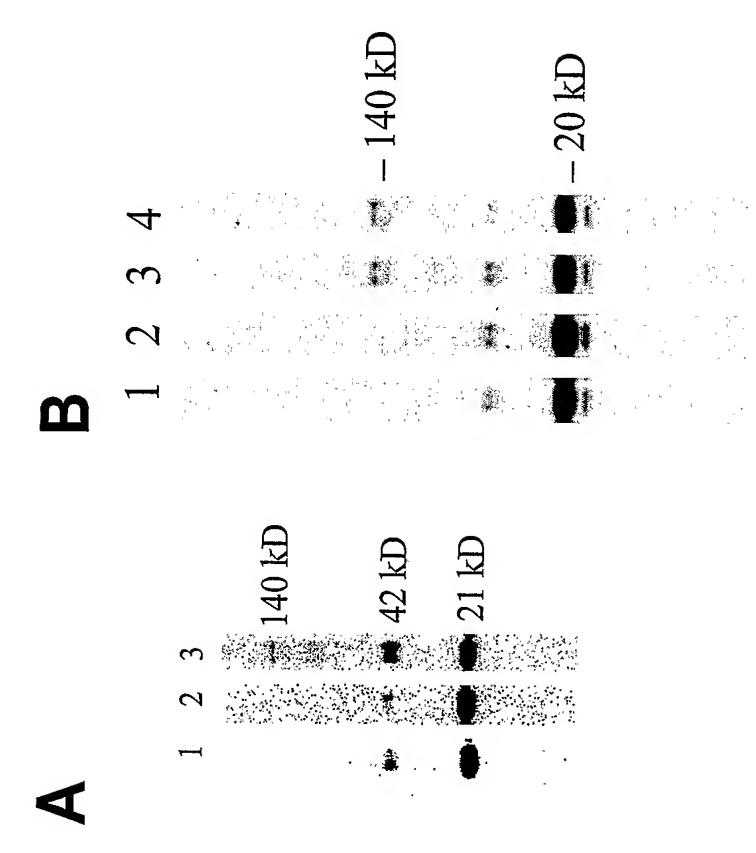


Fig 27



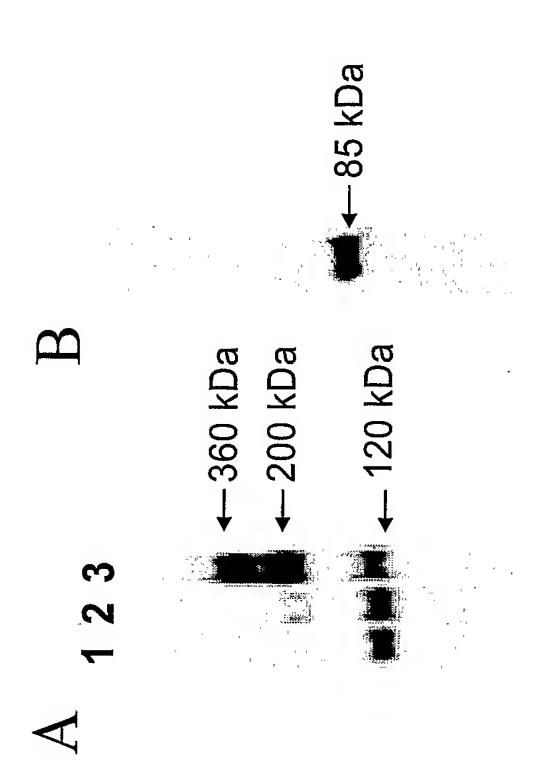


Fig 30

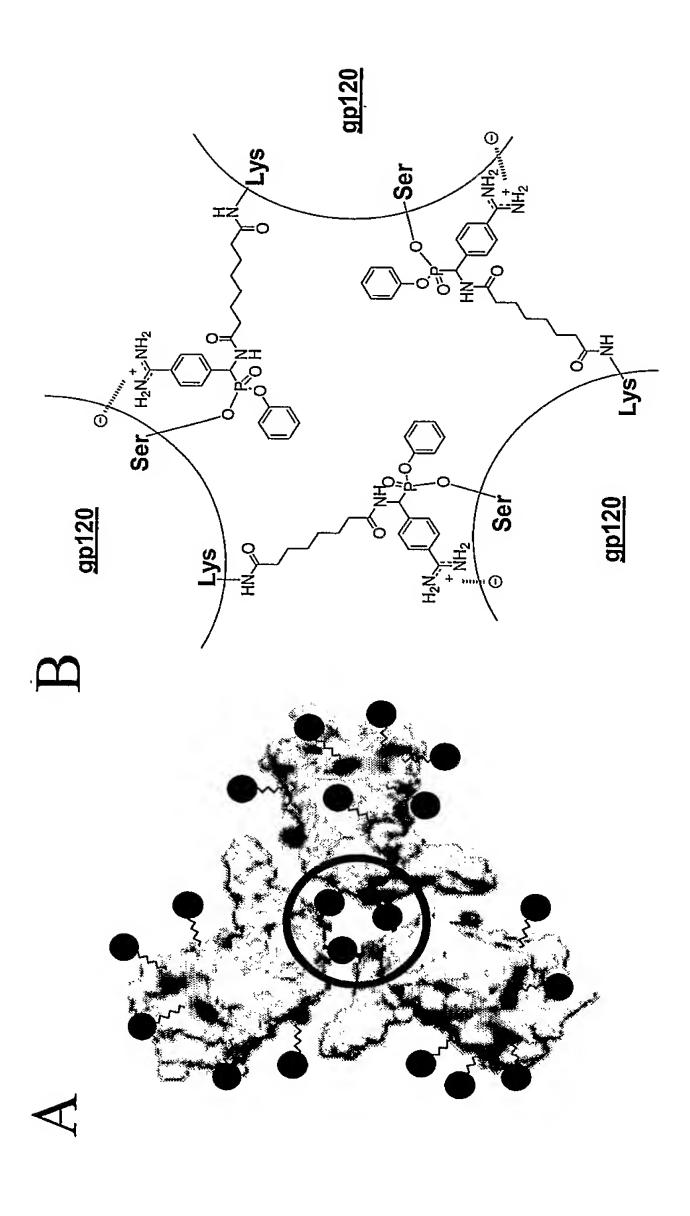


Fig 31

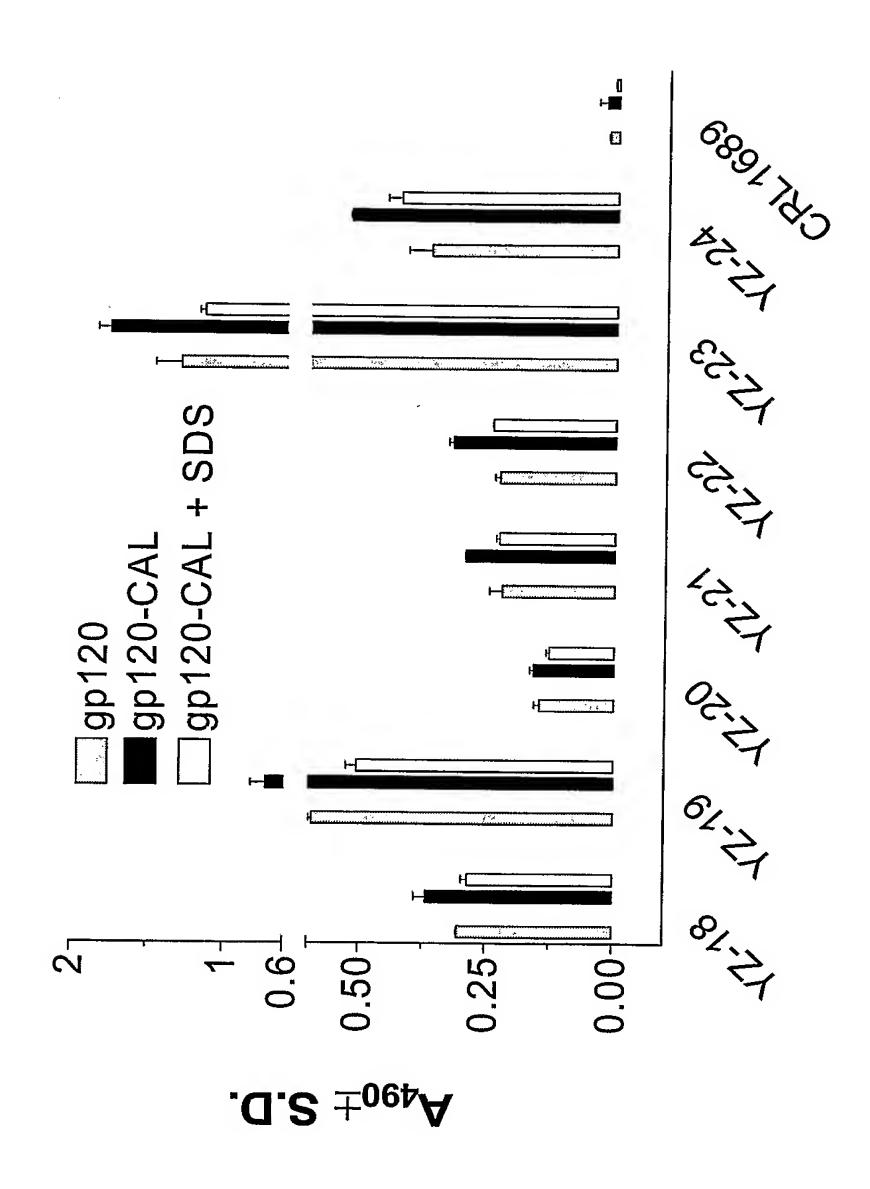


Fig 32

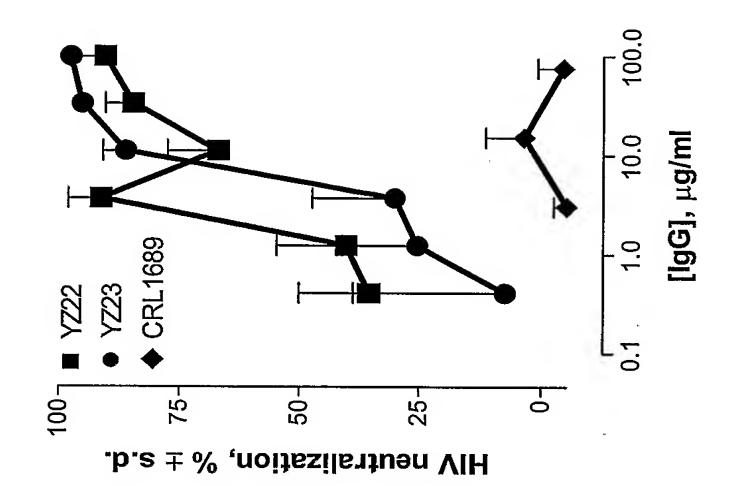


Fig 33